

# Thermoplasticization of Bagasse. I. Preparation and Characterization of Esterified Bagasse Fibers

MOHAMMAD L. HASSAN,<sup>1</sup> ROGER M. ROWELL,<sup>2</sup> NAIM A. FADL,<sup>1</sup> SAMIRA F. YACOUB,<sup>1</sup>  
ALFRED W. CHRISTIANSEN<sup>2</sup>

<sup>1</sup> Cellulose and Paper Department, National Research Center, Dokki, Cairo, Egypt

<sup>2</sup> USDA, Forest Product Laboratory, Madison, Wisconsin 53705

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**ABSTRACT:** This research was to investigate the conversion of bagasse into a thermoplastic material through esterification of the fiber matrix. For this purpose, bagasse was esterified in the absence of solvent using succinic anhydride (SA). The reaction parameters of temperature, reaction time, and amount of succinic anhydride added were studied. Ester content, Fourier transform infrared (FTIR), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and dynamic mechanical thermal analysis (DMTA) were used to characterize the chemical and thermal properties of the esterified fibers. The results showed that on reacting bagasse with SA in the absence of solvent, ester content up to about 48% could be obtained. Diester formation increased with increasing reaction time and temperature at high levels of ester content. Ester content determination of the esterified fibers and their corresponding holocelluloses showed that the reaction took place in the lignin and holocellulose components of bagasse. The IR results showed that the crystallinity index of different esterified bagasse samples did not decrease as a result of increasing the ester content. DSC and TGA results showed that esterified-bagasse fibers were less thermally stable than the untreated fibers, DMTA results showed that esterification of the fibers resulted in a decrease in the  $\tan \delta$  peak temperature of the esterified fibers compared to the untreated fiber. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 561-574, 2000

**Key words:** bagasse; esterification; succinic anhydride; thermoplasticization

## INTRODUCTION

Previous investigators have demonstrated that thermo-moldable products can be produced by extensively modifying wood meal by chemical modification using esterification,<sup>1-28</sup> cyanoethylation,<sup>29-32</sup> allylation,<sup>7,33-35</sup> and etherification<sup>36-42</sup> reactions. The approach of their work was mainly focused on rendering the entire wood structure thermoplastic through chemical modification of wood meal.

Another approach has been adopted by Rowell et al.<sup>21-24</sup> This approach was to modify only the thermoplastic matrix of wood fibers or agro-based fibers (not meal) and to leave the thermoset part as reinforcing filler, that is, to modify lignin and possibly, hemicelluloses—the thermoplastic matrix—and to keep cellulose fibers as reinforcing elements. Using wood fibers or agro-based fibers instead of wood meal has the advantage of utilizing the strength of the fibers.

Dicarboxylic acid anhydrides such as succinic (SA), maleic (MA), and phthalic (PA) anhydrides have been used to esterify wood meal and agro-based fibers with the aim to produce thermo-moldable products. Among these anhydrides, succinic anhydride was found to have the highest

Correspondence to: M. L. Hassan (MLHassan@hotmail.com).  
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reactivity toward wood meal and agro-based fibers.<sup>8,21</sup> Also, succinic anhydride-esterified wood meal was found to have better flow properties than maleic anhydride- and phthalic anhydride-esterified wood.<sup>11,19</sup>

The specific objectives of the present work were to modify bagasse fiber to produce thermoformable composites through chemical modification using succinic anhydride as the esterifying agent. Reaction conditions were selected to modify mainly the matrix of bagasse fiber to lower its glass transition temperature ( $T_g$ ) below the decomposition temperature. A second objective was to characterize the esterified bagasse fibers to determine the optimum reaction conditions to prepare esterified fibers having adequate thermoplasticity with minimum fiber degradation.

## EXPERIMENTAL

### Material Preparation and Esterification

Bagasse (about 2-3 cm long) was hammer milled and screened using a 0.4-mm screen. The fibers were oven dried at 105°C for 6 h and at 65°C overnight. Esterification of bagasse fibers was performed using the following procedure. The desired percent of SA (based on weight of oven-dried fiber) was dissolved in the least possible amount of acetone, typically, for 1 g of SA, 4-5 ml of acetone was required. The SA solution was mixed thoroughly with the fibers to get even distribution of the SA on the fibers. The mixture was left inside a fume hood to allow acetone evaporation and then heated at 100-145°C for 0.25-8 h and 160°C for 0.25-3 h. SA applied to the fiber was from 25% to 200%. The fibers were removed from the oven, and excess SA was removed by Soxhlet extraction using acetone for 4 h. Then, the fibers were dried overnight at 65°C, and weight gains due to esterification were determined based on the original and final oven-dried fiber weights and reported as weight percent gain (WPG).

### Ester Content Determination (Monoester and Diester Contents)

Esterified bagasse samples were ground to pass 40-mesh screen and oven-dried at 100°C for 6 h; the total ester content (monoester and diester content) of SA-modified fibers was calculated from the acid and saponification values of the esterified fibers.<sup>9</sup>

### Holocellulose and $\alpha$ -Cellulose Preparation

Holocellulose preparation was carried out using the sodium chlorite procedure.<sup>43</sup> Residual lignin content of the produced holocellulose was determined using 72% sulfuric acid.<sup>44</sup> TAPPI procedure (T203 os) was used to prepare  $\alpha$ -cellulose from bagasse holocellulose.

### Determination of lignin and Sugars Contents of Bagasse

Sugars contents of bagasse were determined according to the method of Pettersen and Schwandt.<sup>45</sup> Lignin content was determined using the method of Klason.<sup>44</sup>

### Characterization of Esterified Bagasse Fibers

#### Fourier Transform Infrared Analysis

Fourier transform infrared (FTIR) spectroscopy was performed using a Nicolet 6000 spectrophotometer. Samples of each modification were ground to pass 100-mesh screen, oven-dried at 105°C for 6 h, mixed with KBr in a ratio of 1:200 mg (bagasse : KBr) and pressed under vacuum to form pellets. Absorbance was measured over a range from 4000 to 400  $\text{cm}^{-1}$ . For measuring the intensity at a specific wave number, two specimens of each sample were tested, and the results were averaged.

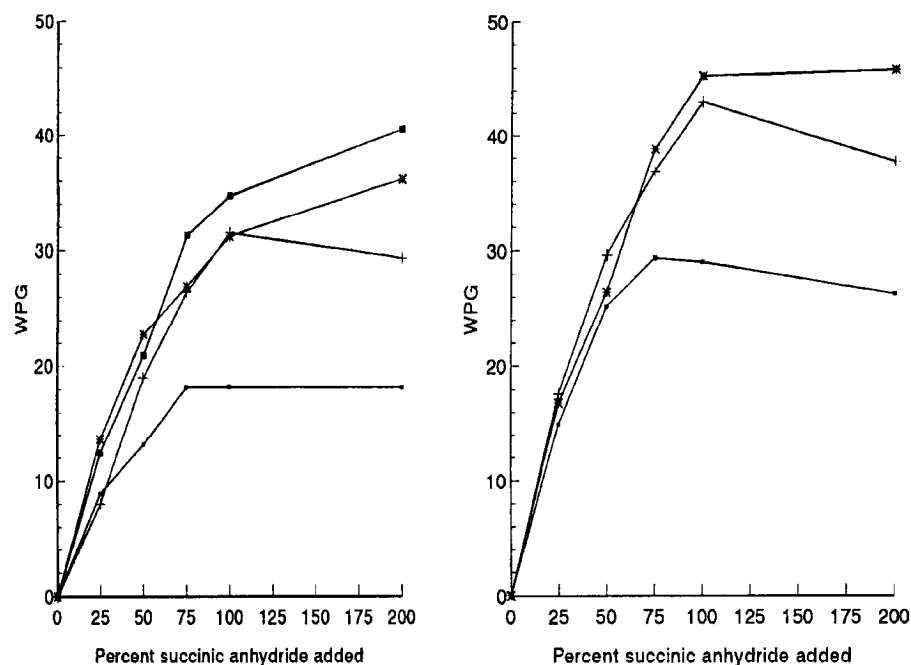
#### Thermogravimetric Analysis and Differential Scanning Calorimetry

Thermogravimetric analysis (TGA) was carried out using an Omnitherm TGA 1000 Thermogravimetric analyzer. An approximately 3-mg sample was used, and the test was carried out under a nitrogen atmosphere at a heating rate of 10°C/min over a temperature range of 50 to 350°C.

The esterified bagasse was thermally analyzed using a Dupont differential scanning calorimeter. The differential scanning calorimetry (DSC) was run on a 3-mg sample uniformly packed in an aluminum pan under a nitrogen atmosphere at a heating rate of 10°C/min over a temperature range of 50 to 350°C. In both TGA and DSC, two specimens of each sample were tested, and the results were averaged.

#### Dynamic Mechanical Thermal Analysis

Softening temperature and thermal transition properties of the esterified bagasse fibers were determined using Rheometric Scientific Mark III



**Figure 1** Effect of the amount of succinic anhydride added on WPG. Reaction time: 1 h (left); 5 h (right). Reaction temperature: (■), 100°C; (+), 130°C; (\*) 145°C; (●), 160°C.

dynamic mechanical thermal analyzer in the compression mode. The oven-dried esterified fibers (about 0.15 g) were pressed into a small pellet of 1.27-cm diameter and about 0.1-cm thickness under high pressure of about 352 MPa at room temperature. The testing temperature of DMTA ranged from 50 to 300°C, the heating rate was 5°C/min, and a frequency of 1 Hz was used. Two specimens of each sample were tested, and the results were averaged.

## RESULTS AND DISCUSSION

### Effect of Reaction Conditions on WPG

The effects of temperature, time, and the amount of SA added on WPG were studied to evaluate the extent of modification achieved on the reaction of bagasse fiber with SA in the absence of solvent or catalyst.

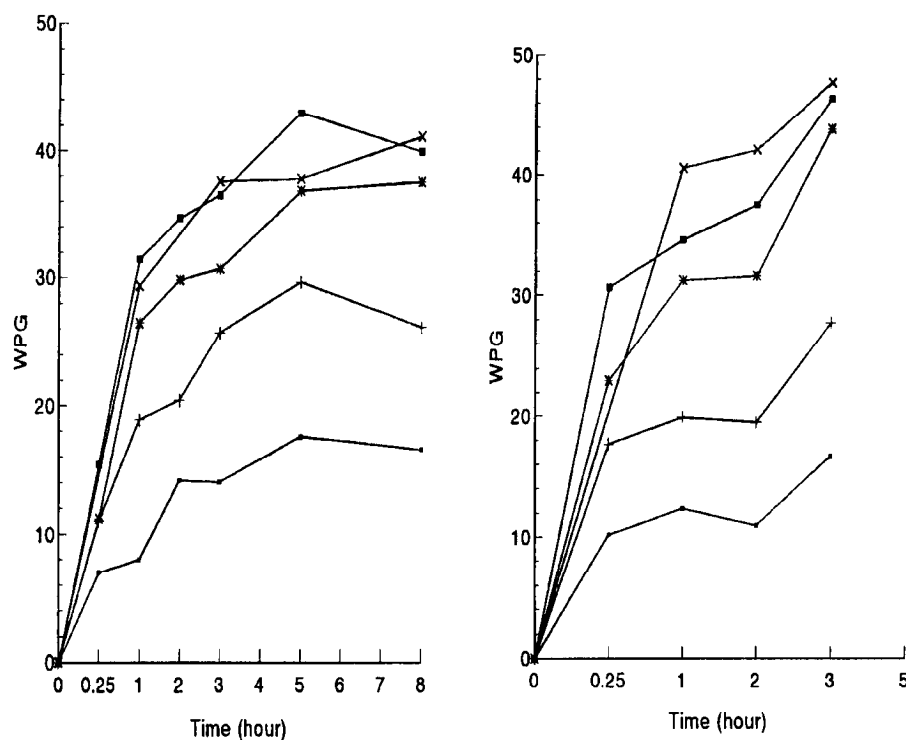
### Effect of the Amount of SA Added on WPG

Figure 1 shows the effect of the amount of SA added on WPG at reaction temperatures from 100 to 160°C for different times. Generally, for reactions at 100–145°C for 1–8 h and at 160°C for 1–3

h, increasing the amount of SA added caused an increase in WPG up to 75–100% of SA addition. Addition of more than 75–100% of SA resulted in relatively small increase in WPG. The maximum WPGs obtained on reacting the fiber with the SA at 100–145°C for 1–8 h and at 160°C for 1–3 h, using 25–200% of SA, were in the range of 40.6–47.8. The maximum WPG obtained was 47.8 when bagasse fiber was reacted with succinic anhydride at 100% SA addition for 3 h at 160°C. In all cases, it was not possible to react entirely all the SA added to bagasse.

### Effect of Reaction Time on WPG

Figure 2 shows the effect of reaction time on WPG at reaction temperatures of 130 and 160°C at different SA additions. Generally, increasing the reaction time more than 2–3 h did not result in significant increases in WPG at 130°C. However, at 160°C there was almost no increase in WPG after 1-h reaction, but after 2 h there was a sudden increase in WPG. This may be due to degradation of the fibers and reaction of the degradation products with SA. Reacting the fibers with SA at 160°C for more than 3 h caused severe degradation of the fibers.



**Figure 2** Effect of reaction time on WPG. Reaction temperature: 130°C (left); 160°C (right). Percent succinic anhydride added: (●), 25% SA; (+), 50% SA; (\*), 75% SA; (■) 100% SA; (x), 200% SA.

#### Effect of Reaction Temperature on WPG

Figure 3 shows the effect of reaction temperature on WPG at reaction times of 1 and 5 h at different SA additions. At a reaction temperature of 100°C (below the melting point of SA), WPGs up to about 29 were obtained at reaction time 5 h. The reactivity of SA in its solid state toward wood meal was found before by Matsuda et al.<sup>9</sup> Increasing the reaction temperature resulted in an increase in WPG. At reaction times of 1 h, the effect of increasing temperature was found to be dependent on the SA amount added. For 25% and 50% SA addition, the increase in temperature had a small effect on WPG, while for 75% or more SA addition, increasing reaction temperature caused significant increase in WPG. For longer reaction times (5 and 8 h) increasing the temperature from 130 to 145°C caused no increase in WPG when 25% to 100% SA were used; at 200% SA, only slight increases in WPG resulted.

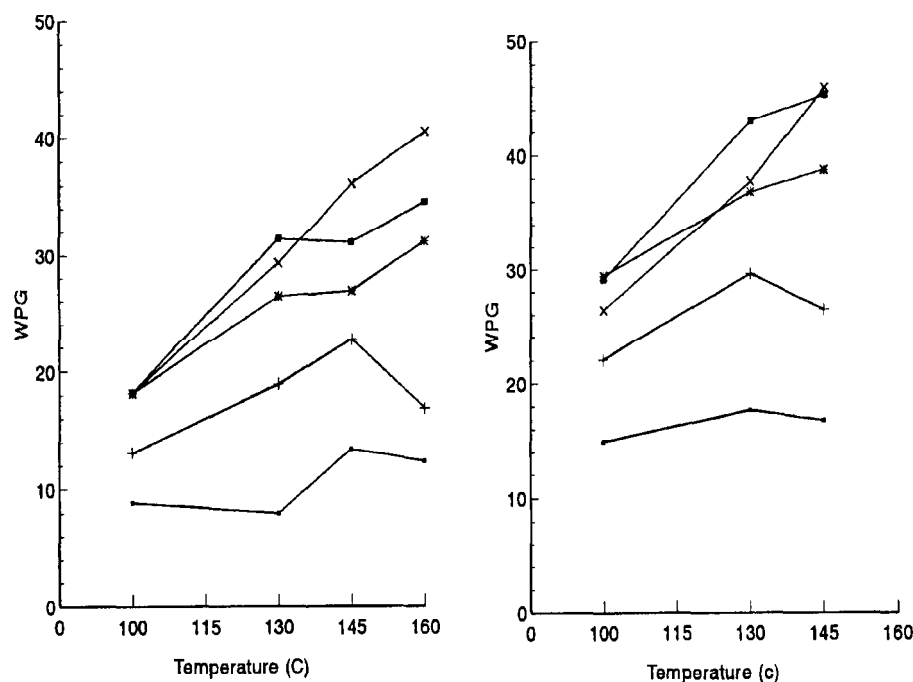
#### Effect of Reaction Conditions on Monoester and Diester Formation

The esterification reaction scheme between bagasse constituent and SA is shown in Figure 4. SA

reacts with hydroxyl groups of bagasse cell wall polymers through an addition reaction by ring opening of the SA. The reaction leads to formation of esterified bagasse-bearing propionyl side chain with free carboxylic acid groups (monoester formation I). However, a crosslinking reaction between the introduced carboxylic acid groups and a second hydroxyl groups of wood has been reported.<sup>9,19</sup> This reaction leads to formation of a diester (II).

Figure 5 shows the effect of reaction temperature on monoester and diester formation after 1 and 5 h of reaction. The monoester content reached a maximum value of 32.7% when bagasse was reacted with 100% SA at 130°C for 1 h. Increasing the reaction temperature more than 130°C and time more than 2 h did not result in an increase in the monoester content but resulted in an increase in total and diester contents. The tendency toward diester formation increased with increasing temperature and time at high total ester contents.

Hon et al.<sup>19</sup> found that at reaction temperature more than 140°C a large amount of diester was formed when wood meal was reacted with SA or MA in absence of solvent, while only monoester



**Figure 3** Effect of reaction temperature on WPG. Reaction time: 1 h (left); 5 h (right). Percent succinic anhydride added: (■), 25% SA; (+), 50% SA; (\*), 75% SA; (●), 100% SA; (×), 200% SA.

was formed when wood was esterified at lower temperature. Clemons et al.<sup>19</sup> found that reacting wood fibers with SA in presence of xylene as a solvent resulted only in monoester formation at the reflux temperature of xylene (about 120°C).

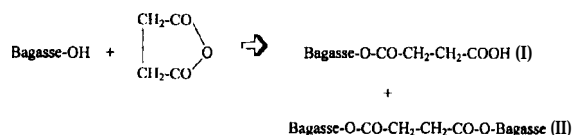
#### Effect of Reaction Conditions on Cellulose and Hemicelluloses Components of Bagasse

The occurrence of degradation in the carbohydrate part of bagasse, that is, hemicelluloses and cellulose, during preparation was briefly tested by determining the holocellulose and  $\alpha$ -cellulose contents of bagasse fibers heated at the different reaction temperatures and times used without adding the SA. The results of holocellulose and  $\alpha$ -cellulose contents of the heat-treated fibers are shown in Table I. A slight decrease in holocellulose content occurred at reaction temperatures of

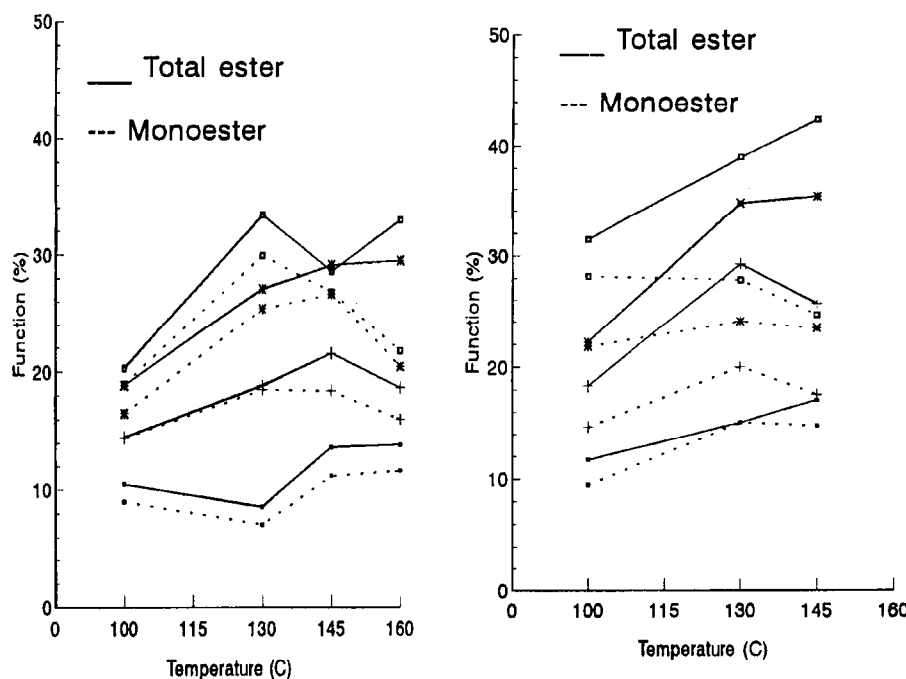
160°C for 3 h and 145°C for 5 h. Otherwise, at lower reaction temperatures and shorter reaction times, no significant effect of reaction temperature and time on holocellulose was found.  $\alpha$ -Cellulose content of the fibers did not change over the reaction temperature and times used.

#### Ester Distribution in Esterified Bagasse Fibers

The distribution of the introduced ester groups in esterified whole bagasse holocellulose and lignin cell wall components was determined by removing lignin from esterified bagasse samples having different WPGs and determining the ester content of the isolated holocelluloses. Rowell et al.<sup>46</sup> reported that the sodium chlorite isolation procedure used did not hydrolyze the ester groups. However, the occurrence of hydrolysis of the ester groups during the isolation of the holocellulose can not be completely ignored.<sup>47</sup> Hydrolysis of some ester groups will cause an error in the determined ester content of the holocelluloses, and consequently in the expected ester content of the lignin component. In addition, residual lignin in the isolated holocelluloses may increase this error. Therefore, the results in this section should be considered as a qualitative determination of



**Figure 4** Reaction scheme between with bagasse fiber constituents and succinic anhydride.



**Figure 5** Effect of reaction conditions on monoester/diester formation. Reaction time: 1 h (left); 5 h (right). Percent succinic anhydride added: (■), 25% SA; (+), 50% SA; (\*), 75% SA; (●), 100% SA.

ester group distribution rather than a quantitative determination.

Table II shows the ester content of different esterified bagasse fiber samples and the corresponding holocelluloses prepared from them. As shown in the table, generally, the prepared holo-

celluloses had ester contents lower than those of their corresponding esterified whole bagasse. This means that the removed lignin contained a considerable amount of ester groups. If the ester groups had attached mainly to the holocellulose parts, the ester content of the holocelluloses would have been found to be more than that of the corresponding esterified whole bagasse.

**Table I** Effect of Reaction Conditions on Holocellulose and  $\mu$ -Cellulose Components of Bagasse Fiber

Reaction Conditions	Holocellulose <sup>a</sup>	$\alpha$ -Cellulose
Raw bagasse	78.3	55.3
130°C, 1 h	79.4	54.4
130°C, 2 h	77.4	56.5
130°C, 3 h	78.7	55.0
130°C, 5 h	79.0	53.8
160°C, 1 h	79.7	54.3
160°C 2 h	79.1	55.8
160°C, 3 h	75.6	54.4
145°C, 3 h	77.8	54.2
145°C, 5 h	74.2	54.0

The fibers were heat-treated at reaction conditions used without succinic anhydride.

<sup>a</sup> Klason lignin content in all holocelluloses was from 2% to 4%.

### Characterization of Esterified Bagasse Fibers

#### FTIR of Esterified-Bagasse Fibers

The chemical structure of esterified bagasse was changed compared to untreated bagasse, as indicated by FTIR spectra (Fig. 6). The intensity of the  $1735\text{-cm}^{-1}$  peak of  $\text{C}=\text{O}$  group due to the acetyl and carboxyl groups of hemicelluloses, and aliphatic ketone or aldehyde in lignin structure increased as a result of the esterification reaction. Also, there was an increase in the intensity of  $\text{C}-\text{O}-\text{C}$  ester stretching band at  $1162\text{ cm}^{-1}$  as a result of the esterification. Figure 7 shows the relation between the increase in the total ester content and the intensities of  $\text{C}=\text{O}$  band at  $1735\text{ cm}^{-1}$ . The  $\text{C}=\text{O}$  absorption intensities were represented by the peak height ratio of the  $\text{C}=\text{O}$  band at  $1735\text{ cm}^{-1}$  to the peak height of the

**Table II Distribution of Ester Groups in Esterified Bagasse Fibers and Chemical Analysis of Bagasse Fiber**

Reaction Conditions	WPG	Ester Content (%) of				
		Whole Bagasse		Holocellulose		
100°C, 3 h	26.1	21.4		20.3		
130°C, 2 h	30.7	35.3		32.1		
130°C, 3 h	36.9	33.9		30.0		
130°C, 5 h	43.9	39.0		32.7		
145°C, 1 h	31.2	29.2		24.4		
145°C, 2 h	34.6	33.6		28.5		
145°C, 3 h	37.4	34.9		29.6		
145°C, 5 h	45.4	42.3		37.1		
160°C, 1 h	34.7	33.9		28.6		
Klason						
Lignin <sup>a</sup>	Arabinose	Galactose	Rhamnose	Glucose	Xylose	Mannose
21.4	1.85	0.55	0.66	42.34	23.95	0.14

<sup>a</sup> Klason lignin content in all holocelluloses was from 2% to 3%.

aromatic ring stretching band at 1514 cm<sup>-1</sup> (internal standard band). Increasing the total ester content resulted in an increase in the peak height ratio, that is, increase in C=O band intensities. The coefficient of correlation (*R*) of the curves shows a good degree of correlation between the peak height ratio and the total ester content; the high coefficient of determination (*R*<sup>2</sup>) shows a fairly good linear fit. The values of *R* and *R*<sup>2</sup> were in the range of 0.86–0.91 and 0.74–0.79, respectively.

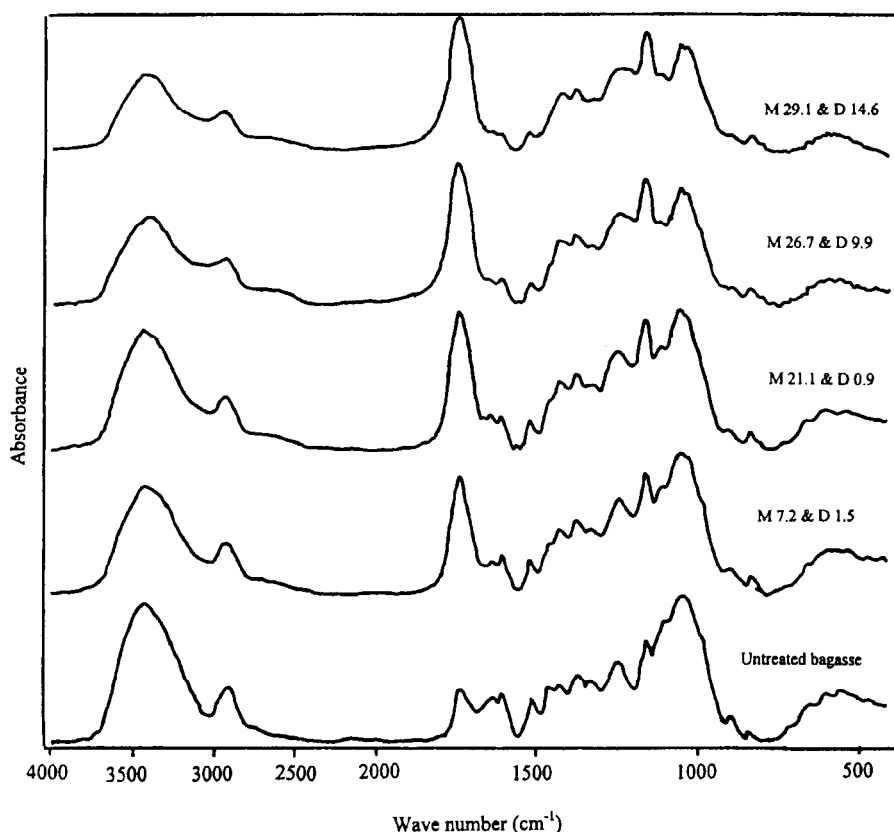
IR spectra have been used to determine the degree of crystallinity and crystalline modification of pure celluloses.<sup>48–52</sup> The intensity of certain bands in IR spectra have been found to be sensitive to variations in cellulose crystallinity or crystalline form. Such variation may be determined using the ratio of a band that is affected by cellulose crystallinity to that of a band that is comparatively insensitive to crystallinity changes. The ratio of the absorbency of the peaks at 1429 cm<sup>-1</sup> to those at 894 cm<sup>-1</sup> (*A*<sub>1429</sub>/*A*<sub>894</sub>)<sup>48</sup> and *A*<sub>1372</sub>/*A*<sub>2900</sub><sup>49,50</sup> have been used to measure the relative cellulose crystallinity, and *A*<sub>1370</sub>/*A*<sub>690</sub> (the ratio of the combined areas of the peaks at 1370, 1335, and 1315 cm<sup>-1</sup> to that of 690 cm<sup>-1</sup> band) has been used for investigation of the transformation of cellulose I and cellulose II.<sup>51,52</sup>

Table III shows the crystallinity index (CrI) of esterified bagasse fiber samples calculated using the different mentioned measures. As shown in

the table, there is no decrease in the CrI of the esterified samples on increasing the ester content from 8.7% to 43.7%. This should mean that the esterification occurred mainly in the amorphous region of bagasse, probably due to the absence of solvent or swelling agent. Taking also into consideration the accessibility of the hydroxyl groups in the amorphous region leads to the expectation that esterification occurred to a larger extent in hemicellulose and lignin components than in the cellulose component. As mentioned in the previous section, it was found that lignin was esterified to a considerable extent although it has only 1.16 hydroxyl group per phenyl propane unit as compared to cellulose and hemicelluloses, which have 3 and 2–3 hydroxyl groups per unit, respectively.

#### TGA and DSC of Esterified Bagasse Fibers

TGA and DSC were used to study thermal stability of esterified bagasse fibers in the temperature range from 50 to 350°C. TGA curves of esterified bagasse fibers showed that esterified bagasse fibers were less thermally stable than the untreated fibers, as seen in Figure 8. Table IV summarizes the TGA results of untreated and esterified bagasse fibers. Untreated bagasse had an initial weight loss temperature of 233°C and maximum weight loss temperature of 314°C. The initial weight loss at 233°C is probably due to generation of noncombustible gases such as CO, CO<sub>2</sub>,



**Figure 6** FTIR spectra of untreated and esterified bagasse samples. M, monoester content; D, diester content.

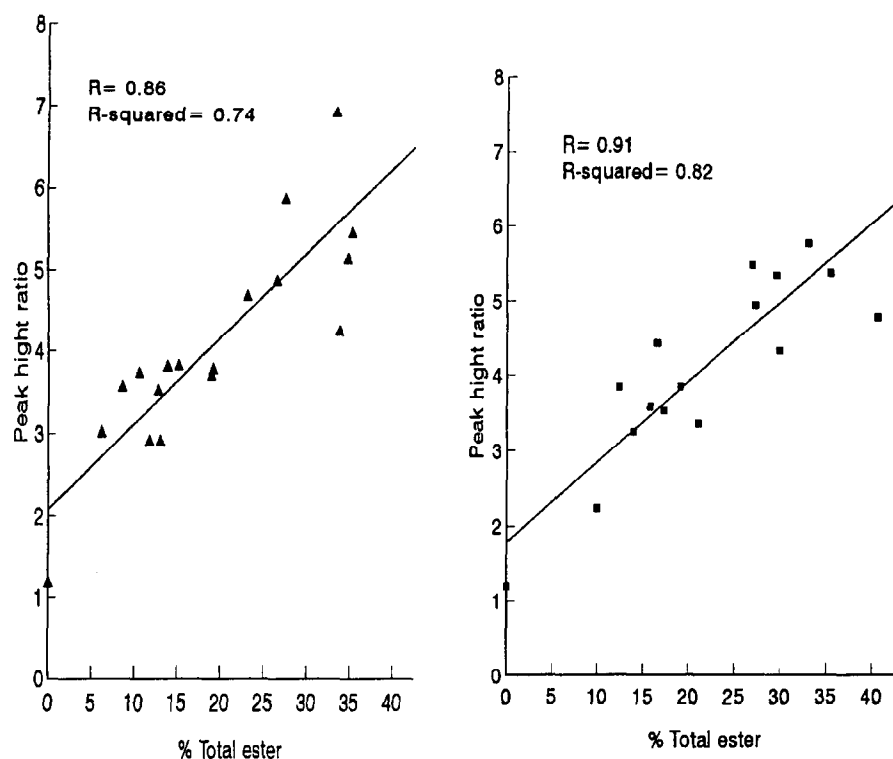
formic acid, and acetic acid, whereas the significant weight loss at 314°C indicates the onset of pyrolysis and generation of combustible gases.<sup>53</sup> Esterified bagasse fibers had an initial weight loss temperature range of 181–189°C and maximum weight loss temperature range of 250–261°C, depending on their ester contents. Also, another weight loss was observed at 314°C due to the onset of pyrolysis, which is very comparable to that of the untreated bagasse. The initial weight loss at 181–189°C may be due to de-carboxylation of the introduced carboxyl groups.<sup>19</sup> Increasing the total ester or the monoester content resulted in a decrease in both of the initial weight loss temperature and the maximum weight loss temperature. These results indicate a de-carboxylation reaction of the pendent carboxyl groups or a de-esterification reaction followed by de-carboxylation or both. The lower stability of esterified wood as compared to the untreated wood meal was reported before for woods treated with SA, MA, and PA.<sup>11,25</sup>

Figure 9 shows DSC diagrams of untreated and esterified bagasse fiber samples. DSC of un-

treated bagasse fiber showed a small exothermic peak at 330°C and an endothermic peak at 360°C. The exothermic peak may be due to the thermal decomposition of hemicelluloses and cleavage of the glycosidic bonds of cellulose<sup>54</sup> as well as the decomposition of lignin.<sup>55</sup> The endothermic peak at 360°C may be attributed to the fission of sugar unites, which provides a variety of carbonyl compounds such as acetaldehyde, glyoxal, and acrolein. These compounds readily evaporate resulting in an endothermic peak in the DSC.<sup>56</sup>

On the other hand, DSC diagrams of esterified bagasse fibers showed two endothermic peaks. The first peak was at 250°C and the second at 360°C. The first endothermic peak may be due to the de-carboxylation reaction of the esterified bagasse,<sup>19</sup> while the second endothermic peak at 360°C is similar to that of the untreated bagasse. This may suggest that esterification of bagasse does not affect the pyrolysis of bagasse main components. As shown, all the esterified samples had the same DSC pattern but the area of the endothermic peak centered at 250°C increased as the total ester content increased, that is, the enthalpy





**Figure 7** Effect of total ester content of the esterified-bagasse fibers on the intensity of the C=O band. Reaction temperature and time, respectively: 130°C and 0.25–5 h (left); 160°C and 0.25–3 h (right).

change (AH) increased as the total ester content increased. This indicates that the endothermic reaction occurred mainly on the introduced ester chains. This is clear in Table V, which shows the data of DSC diagrams of several esterified bagasse samples. Increasing the total ester content did not affect AH of the peak at 360°C, which is due to pyrolysis of bagasse.

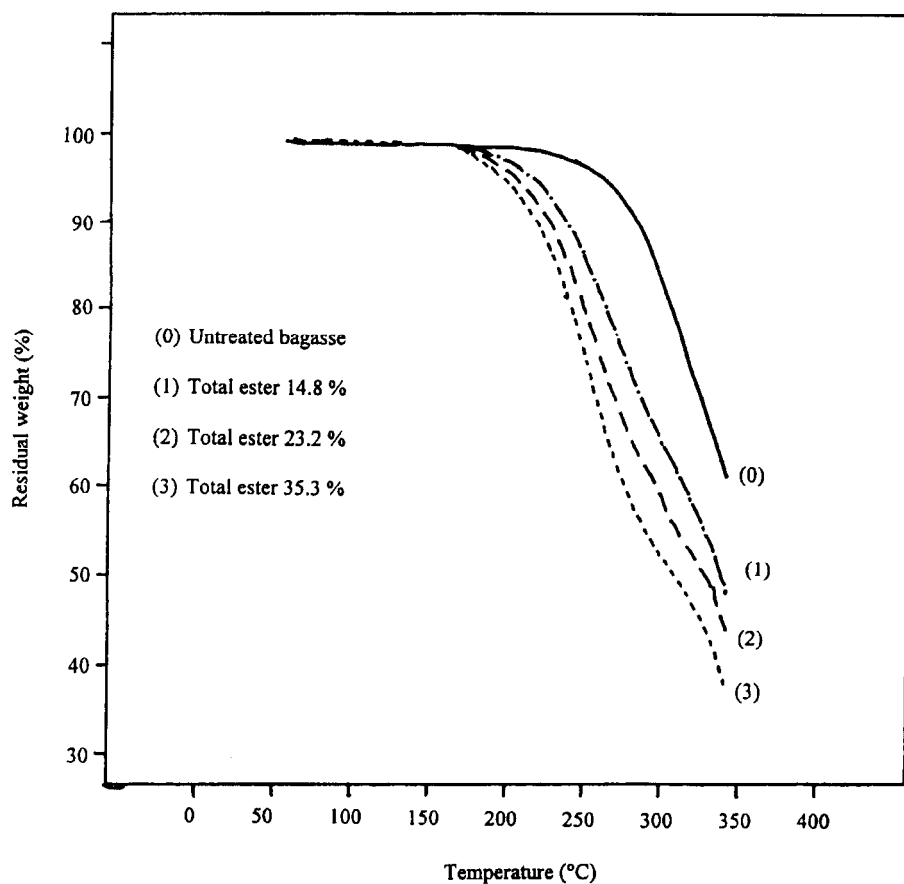
#### DMTA of Esterified Bagasse Fibers

DMTA of polymers shows some basic mechanical properties such as dynamic modulus, damping factor, and thermal transitions.<sup>57</sup> The dynamic modulus is the most basic of all mechanical properties, and the mechanical damping ( $\tan \delta$ ) is often the most sensitive indicator of molecular

**Table III** Effect of Esterification on CrI of Bagasse Fiber

Ester Content	CrI $A_{1372}/A_{2900}$	CrI $A_{1429}/A_{894}$	CrI $A_{1370}/A_{670}$
Raw bagasse	1.24	2.21	1.85
8.7	1.49	2.70	2.35
13.8	1.51	2.89	2.77
22.0	1.43	2.93	2.45
32.9	1.54	3.31	3.89
35.2	1.53	3.0	2.84
36.6	1.51	3.28	3.86
43.7	1.47	2.21	3.53

CrI, crystallinity index.



**Figure 8** TGA of untreated and esterified bagasse fiber samples.

motions, even in the solid state. The dynamic modulus and the damping factor are functions of temperature. The storage modulus  $E'$  is defined as the stress in phase with the strain in a sinusoidal shear deformation divided by strain; it is a

measure of the energy stored and recovered per cycle when different systems are compared at the same strain amplitude. The loss modulus  $E''$  is defined as the stress  $90^\circ$  out of phase with the strain divided by the strain; it is a measure of the

**Table IV** TGA Results of Esterified Bagasse Fibers

Ester Content (Monoester and Diester)	Initial Weight Loss Temp (°C)	Extrapolation Onset Temp (°C) <sup>a</sup>	Maximum Weight Loss Temp (°C)	Weight Loss at 233°C (%) <sup>b</sup>
Untreated bagasse	233	264	314	0
M, 13.64; D, 0.19	189	223	261	7.82
M, 16.98; D, 2.15	187	215	256	11.06
M, 18.09; D, 5.07	187	218	252	11.58
M, 32.65; D, 2.65	181	212	254	15.11
M, 27.32; D, 6.46	181	211	251	13.57
M, 21.81; D, 11.14	189	217	254	12.05

<sup>a</sup> Extrapolation onset is the intersection of two lines that are tangent to the curve in the linear region.

<sup>b</sup> Percentage weight loss at 233°C indicates percentage weight loss before initial weight loss temperature of untreated bagasse. M, monoester content (%); D, diester content (%).

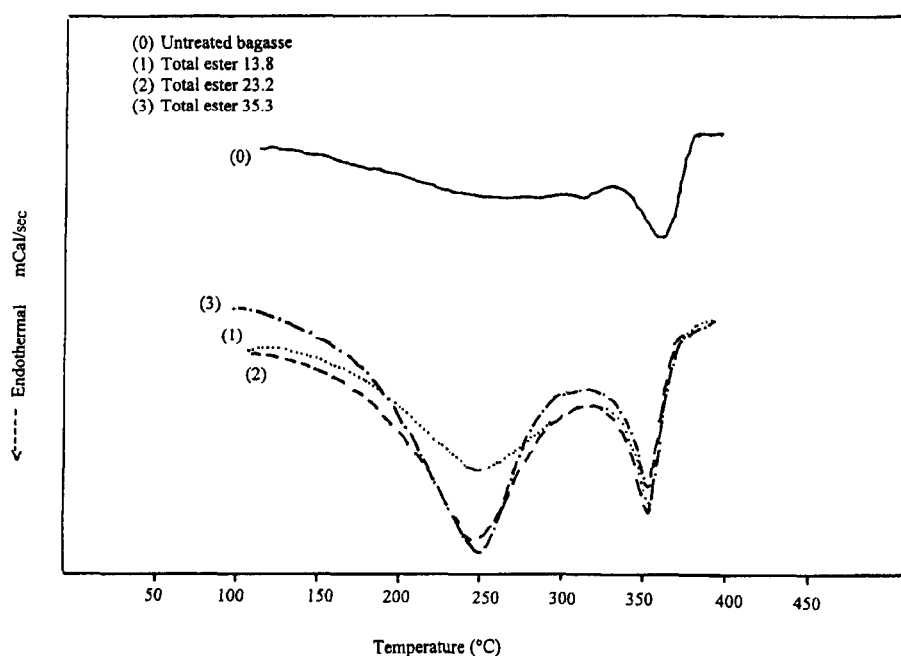


Figure 9 DSC of untreated and esterified bagasse fiber samples.

energy dissipated or lost as heat per cycle of sinusoidal deformation. The damping factor  $\tan \delta$  is a measure of the ration of energy lost to energy stored in a cyclic deformation, that is,  $\tan \delta = E''/E'$ .

Figure 10 shows the DMTA diagrams of untreated bagasse and esterified bagasse fiber samples with different total ester contents. The  $\tan \delta$  peaks indicate the onset of the molecular motion of large segments of the polymeric components of bagasse (glass transition temperature), the glass transition temperature of dry wood cellulose and hemicellulose occurs in the same region.<sup>58,59</sup> The

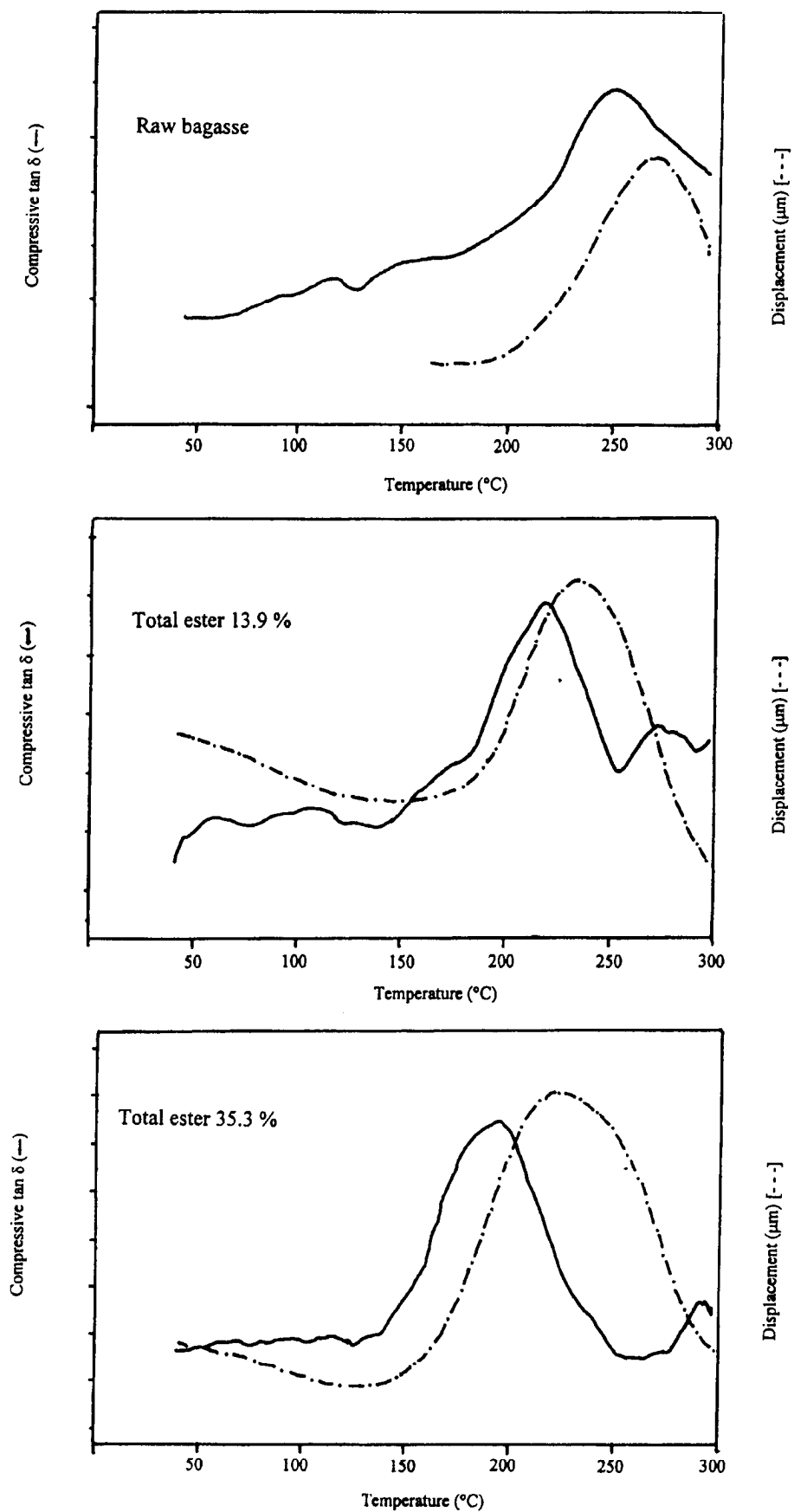
displacement peaks indicate occurrence of softening of bagasse as a whole (softening temperature).

Table VI summarizes DMTA data of esterified bagasse fiber samples with different monoester and diester contents. Increasing the total ester content resulted in a decrease in  $\tan \delta$  and the softening temperature up to 32% ester content; however, no change in both  $\tan \delta$  and the softening temperature at total ester content of more than about 32% was observed. Untreated bagasse had  $\tan \delta$  peak temperature at 252°C, which is above the initial weight loss temperature of raw bagasse, as found in the TGA results, while ester-

Table V DSC Results of Esterified-Bagasse Fibers

Total Ester Content of the Esterified Bagasse Fibers (%)	$\Delta H$ (mcal/mg) of the Peak at 360°C	$\Delta H$ (mcal/mg) of the Peak at 250°C
Untreated bagasse	7.42	—
6.2 (M, 5.0; D, 1.2)	11.47	17.66
13.8 (M, 13.6; D, 0.2)	10.90	23.70
19.1 (M, 17.0; D, 2.1)	12.92	32.50
22.2 (M, 21.8; D, 1.4)	13.18	32.2
35.3 (M, 32.7; D, 2.6)	9.60	45.11
33.8 (M, 27.3; D, 6.5)	11.90	51.80
35.5 (M, 21.8; D, 13.7)	11.50	50.62

M, monoester content (%); D, diester content (%).



**Figure 10** DMTA of untreated and esterified bagasse fiber samples.

**Table VI DMTA Results of Esterified-Bagasse Fibers**

Total Ester Content	Preparation Conditions	Softening Temperature (°C)	Tan $\delta$ Peak Temperature (°C)
Untreated bagasse	None	268	252
6.2 (M, 5.0; D, 1.2)	145°C, 0.25 h	237	225
8.6 (M, 7.1; D, 1.5)	130°C, 1 h	235	221
13.9 (M, 11.7; D, 2.2)	160°C, 1 h	233	219
19.2 (M, 17.0; D, 2.2)	130°C, 1 h	225	214
27.5 (M, 26.5; D, 1.0)	100°C, 3 h	220	205
32.4 (M, 21.3; D, 11.1)	160°C, 1 h	222	197
35.3 (M, 32.7; D, 2.6)	130°C 2 h	224	199
42.5 (M, 24.7; D, 17.8)	145°C, 5 h	223	197

M, monoester content (%); D, diester content (%).

ified bagasse samples had tan  $\delta$  peak temperature from 197 to 225°C depending on their total ester content. Esterified bagasse fiber samples, which had ester content about 6–14%, showed a tan  $\delta$  peak temperature range at 219–225°C, that is, below the initial weight loss temperature of raw bagasse (233°C). This means that even low levels of esterification resulted in a decrease in tan  $\delta$  peak temperature from 252°C to 219–225°C. Esterified bagasse samples that had total ester content about 27–42% showed a tan  $\delta$  peak temperature range from 197 to 206°C. The esterified bagasse sample, which was prepared by reacting bagasse fibers with the anhydride at 100°C (below the melting point of the anhydride) had a tan  $\delta$  and softening temperatures at 205 and 220°C, respectively. The tan  $\delta$  peak temperatures of all esterified bagasse samples were higher than the initial weight loss temperatures of these fibers, as seen from TGA results. So, the effect of this weight loss of esterified bagasse sample during the DMTA scan can not be neglected, and consequently, the appearance of the tan  $\delta$  peaks of the esterified fibers lower than that of raw bagasse can not be considered as a clear evidence of plasticization of esterified bagasse.

## CONCLUSIONS

Although bagasse was esterified up to weight gain of about 48%, using DMTA could not clearly proof the occurrence of plasticization of the esterified fibers. The tan  $\delta$  peak temperatures for various esterified samples appeared above the temperature region of the remarkable weight decrease

found in TGA of these samples. In the part II of this work,<sup>60</sup> scanning electron microscopy of composites prepared from the esterified fibers without adhesive will be carried out to follow the effect of esterification on thermoplasticity of these fibers.

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